US009252426B2

(12) **United States Patent**
Green

(10) **Patent No.: US 9,252,426 B2**
(45) **Date of Patent: Feb. 2, 2016**

(54) **SILICON ANODE FOR A RECHARGEABLE BATTERY**

(75) Inventor: **Mino Green**, London (GB)

(73) Assignee: **Nexeon Limited**, Oxfordshire (GB)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 536 days.

(21) Appl. No.: **12/599,034**

(22) PCT Filed: **May 9, 2008**

(86) PCT No.: **PCT/GB2008/001604**

§ 371 (c)(1),
(2), (4) Date: **Feb. 26, 2010**

(87) PCT Pub. No.: **WO2008/139157**

PCT Pub. Date: **Nov. 20, 2008**

(65) **Prior Publication Data**

US 2010/0190061 A1 Jul. 29, 2010

(30) **Foreign Application Priority Data**

May 11, 2007 (GB) 0709165.5

(51) **Int. Cl.**

H01M 4/58	(2010.01)
H01M 4/88	(2006.01)
H01M 4/38	(2006.01)
H01M 4/134	(2010.01)
H01M 4/1395	(2010.01)
H01M 4/525	(2010.01)
H01M 10/052	(2010.01)

(52) **U.S. Cl.**

CPC ***H01M 4/38*** (2013.01); *H01M 4/134* (2013.01); *H01M 4/1395* (2013.01); *H01M 4/525* (2013.01); *H01M 10/052* (2013.01); *Y02E 60/122* (2013.01)

(58) **Field of Classification Search**

USPC 429/231.95

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,351,445	A	11/1967	Fielder et al.
4,002,541	A	1/1977	Streander
4,436,796	A	3/1984	Huggins et al.
4,950,566	A	8/1990	Huggins et al.
5,260,148	A	11/1993	Idota

(Continued)

FOREIGN PATENT DOCUMENTS

CN	1447916	A	10/2003
CN	101442124	A	5/2009

(Continued)

OTHER PUBLICATIONS

Chan et al., "Surface Chemistry and Morphology of the Solid Electrolyte Interphase on Silicon Nanowire Lithium-Ion Battery Anodes", Journal of Power Sources, 189(2), 1132-1140, (2009).

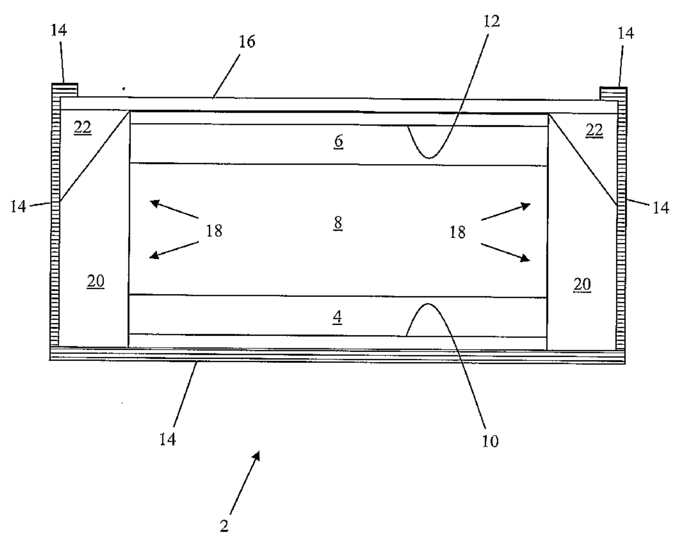
(Continued)

Primary Examiner — Ula C Ruddock
Assistant Examiner — Osei Amponsah
(74) *Attorney, Agent, or Firm* — McDonnell Boehnen Hulbert & Berghoff LLP

(57) **ABSTRACT**

An electrode and electrode assembly, for example for use as an anode in a lithium-ion rechargeable cell that uses silicon or silicon-based elements of specific dimensions and geometry as its active material, is provided, as well as methods for manufacturing the same. The active silicon or silicon-based material may include fibers, sheets, flakes, tubes or ribbons, for example.

22 Claims, 1 Drawing Sheet



(56) **References Cited**

U.S. PATENT DOCUMENTS

5,262,021	A	11/1993	Lehmann et al.
5,660,948	A	8/1997	Barker
5,907,899	A	6/1999	Dahn et al.
5,980,722	A	11/1999	Kuroda et al.
6,022,640	A	2/2000	Takada et al.
6,042,969	A	3/2000	Yamada et al.
6,063,995	A	5/2000	Bohland et al.
6,235,427	B1 *	5/2001	Idota et al. 429/218.1
6,296,969	B1	10/2001	Yano et al.
6,334,939	B1	1/2002	Zhou et al.
6,337,156	B1	1/2002	Narang et al.
6,353,317	B1	3/2002	Green et al.
6,399,177	B1	6/2002	Fonash et al.
6,399,246	B1	6/2002	Vandayburg et al.
6,432,579	B1 *	8/2002	Tsuji et al. 429/218.1
6,589,696	B2	7/2003	Matsubara et al.
6,605,386	B1	8/2003	Kasamatsu et al.
6,620,547	B1	9/2003	Sung et al.
6,887,511	B1	5/2005	Shima et al.
6,916,679	B2	7/2005	Snyder et al.
7,033,936	B1	4/2006	Green
7,051,945	B2	5/2006	Empedocles et al.
7,070,632	B1	7/2006	Visco et al.
7,094,499	B1	8/2006	Hung
7,147,894	B2	12/2006	Zhou et al.
7,192,673	B1	3/2007	Ikeda et al.
7,311,999	B2	12/2007	Kawase et al.
7,318,982	B2	1/2008	Gozdz et al.
7,348,102	B2	3/2008	Li et al.
7,358,011	B2	4/2008	Fukuoka et al.
7,378,041	B2	5/2008	Asao et al.
7,425,285	B2	9/2008	Asao et al.
7,476,469	B2	1/2009	Ota et al.
7,569,202	B2	8/2009	Farrell et al.
7,659,034	B2	2/2010	Minami et al.
7,674,552	B2	3/2010	Nakai et al.
7,767,346	B2	8/2010	Kim et al.
7,862,933	B2	1/2011	Okumura et al.
8,034,485	B2	10/2011	Dahn et al.
2001/0023986	A1	9/2001	Mancevski
2002/0074972	A1 *	6/2002	Narang et al. 320/131
2002/0121460	A1 *	9/2002	Moy et al. 208/133
2003/0135989	A1	7/2003	Huggins et al.
2004/0072067	A1	4/2004	Minami et al.
2004/0126659	A1 *	7/2004	Graetz et al. 429/218.1
2004/0151987	A1	8/2004	Kawase et al.
2004/0166319	A1	8/2004	Li et al.
2004/0185346	A1	9/2004	Takeuchi et al.
2004/0197660	A1	10/2004	Sheem et al.
2004/0214085	A1	10/2004	Sheem et al.
2004/0224231	A1	11/2004	Fujimoto et al.
2004/0241548	A1	12/2004	Nakamoto et al.
2005/0042515	A1	2/2005	Hwang et al.
2005/0079414	A1	4/2005	Yamamoto et al.
2005/0079420	A1	4/2005	Cho et al.
2005/0118503	A1	6/2005	Honda et al.
2005/0191550	A1	9/2005	Satoh et al.
2005/0193800	A1	9/2005	DeBoer et al.
2005/0214644	A1	9/2005	Aramata et al.
2006/0003226	A1	1/2006	Sawa et al.
2006/0004226	A1	1/2006	Machhammer et al.
2006/0019115	A1	1/2006	Wang et al.
2006/0019168	A1	1/2006	Li et al.
2006/0024582	A1	2/2006	Li et al.
2006/0051670	A1	3/2006	Aramata et al.
2006/0057463	A1	3/2006	Gao et al.
2006/0088767	A1	4/2006	Li et al.
2006/0097691	A1 *	5/2006	Green 320/107
2006/0134516	A1	6/2006	Im et al.
2006/0134518	A1	6/2006	Kogetsu et al.
2006/0147800	A1	7/2006	Sato et al.
2006/0154071	A1	7/2006	Homma et al.
2006/0166093	A1	7/2006	Zaghib et al.
2006/0175704	A1	8/2006	Shimizu et al.
2006/0257307	A1	11/2006	Yang
2006/0263687	A1	11/2006	Leitner et al.
2006/0275663	A1	12/2006	Matsuno et al.
2006/0275668	A1	12/2006	Peres et al.
2006/0286448	A1	12/2006	Snyder et al.
2007/0020521	A1 *	1/2007	Obrovac et al. 429/218.1
2007/0026313	A1	2/2007	Sano
2007/0031733	A1	2/2007	Kogetsu et al.
2007/0037063	A1	2/2007	Choi et al.
2007/0048609	A1	3/2007	Yeda et al.
2007/0059598	A1	3/2007	Yang
2007/0065720	A1	3/2007	Hasewaga et al.
2007/0072074	A1	3/2007	Yamamoto et al.
2007/0087268	A1	4/2007	Kim et al.
2007/0099084	A1	5/2007	Huang et al.
2007/0099085	A1	5/2007	Choi et al.
2007/0105017	A1	5/2007	Kawase et al.
2007/0117018	A1	5/2007	Huggins
2007/0122702	A1	5/2007	Sung et al.
2007/0148544	A1	6/2007	Le
2007/0172732	A1	7/2007	Jung et al.
2007/0184345	A1	8/2007	Neudecker et al.
2007/0190413	A1	8/2007	Lee et al.
2007/0202395	A1	8/2007	Snyder et al.
2007/0202402	A1	8/2007	Asahina et al.
2007/0207080	A1	9/2007	Yang
2007/0207385	A1	9/2007	Liu et al.
2007/0209584	A1	9/2007	Kalynushkin et al.
2007/0212538	A1	9/2007	Niu
2007/0218366	A1	9/2007	Kalynushkin et al.
2007/0224508	A1	9/2007	Aramata et al.
2007/0224513	A1	9/2007	Kalynushkin et al.
2007/0238021	A1	10/2007	Liu et al.
2007/0243469	A1	10/2007	Kim et al.
2007/0264564	A1	11/2007	Johnson et al.
2007/0264574	A1	11/2007	Kim et al.
2007/0269718	A1	11/2007	Krause et al.
2007/0277370	A1	12/2007	Kalynushkin et al.
2008/0003496	A1	1/2008	Neudecker et al.
2008/0003503	A1	1/2008	Kawakami et al.
2008/0020281	A1	1/2008	Kogetsu et al.
2008/0038638	A1	2/2008	Zhang et al.
2008/0044732	A1 *	2/2008	Salot et al. 429/322
2008/0090149	A1	4/2008	Sano et al.
2008/0096110	A1	4/2008	Bito et al.
2008/0107967	A1	5/2008	Liu et al.
2008/0113271	A1	5/2008	Ueda et al.
2008/0118834	A1	5/2008	Yew et al.
2008/0124631	A1	5/2008	Fukui et al.
2008/0131782	A1	6/2008	Hagiwara et al.
2008/0138710	A1	6/2008	Liaw et al.
2008/0138716	A1	6/2008	Iwama et al.
2008/0145752	A1	6/2008	Hirose et al.
2008/0145759	A1	6/2008	Sung et al.
2008/0160415	A1	7/2008	Wakita et al.
2008/0176139	A1	7/2008	White et al.
2008/0206631	A1	8/2008	Christensen et al.
2008/0206641	A1	8/2008	Christensen et al.
2008/0233479	A1	9/2008	Sung et al.
2008/0233480	A1	9/2008	Sung et al.
2008/0241647	A1	10/2008	Fukui et al.
2008/0241703	A1	10/2008	Yamamoto et al.
2008/0248250	A1	10/2008	Flemming et al.
2008/0261112	A1	10/2008	Nagata et al.
2008/0305391	A1	12/2008	Hirose et al.
2009/0053589	A1	2/2009	Obrovac et al.
2009/0078982	A1	3/2009	Rachmady et al.
2009/0087731	A1	4/2009	Fukui et al.
2009/0101865	A1	4/2009	Matsubara et al.
2009/0117466	A1	5/2009	Zhamu et al.
2009/0186267	A1	7/2009	Tiegs
2009/0239151	A1	9/2009	Nakanishi et al.
2009/0253033	A1	10/2009	Hirose et al.
2009/0269677	A1	10/2009	Hirose et al.
2009/0305129	A1	12/2009	Fukui et al.
2010/0085685	A1	4/2010	Pinwill
2010/0092868	A1	4/2010	Kim et al.
2010/0124707	A1	5/2010	Hirose et al.
2010/0136437	A1	6/2010	Nishida et al.
2010/0151324	A1 *	6/2010	Green et al. 429/220

(56) **References Cited**

U.S. PATENT DOCUMENTS

2010/0285358	A1	11/2010	Cui et al.
2010/0297502	A1	11/2010	Zhu et al.
2010/0330419	A1	12/2010	Cui et al.

FOREIGN PATENT DOCUMENTS

DE	199 22 257	A1	11/2000		
DE	103 47 570	A1	5/2005		
EP	0 281 115		9/1988		
EP	0 553 465	A1	8/1993		
EP	0 553 465	A1	8/1993		
EP	0 820 110	A2	1/1998		
EP	1 011 160	A1	6/2000		
EP	0 936 687	B1	12/2001		
EP	1 231 653	A1	8/2002		
EP	1 231 654	A1	8/2002		
EP	1 258 937	A1	11/2002		
EP	1 083 614	B1	5/2003		
EP	1 313 158	A2	5/2003		
EP	1 335 438	A1	8/2003		
EP	1 289 045	B1	3/2006		
EP	1 657 769	A1	5/2006		
EP	1 850 409	A1	10/2007		
EP	1 771 899	B1	2/2008		
EP	1 657 768	B1	5/2008		
EP	2 058 882		5/2009		
EP	2 204 868	A3	7/2010		
FR	2 885 913	B1	8/2007		
GB	980513		1/1965		
GB	1 014 706		12/1965		
GB	2 395 059	A	5/2004		
GB	2 464 157	B	1/2010		
GB	2 464 158		4/2010		
JP	02-209492	A	8/1990		
JP	6-283156		10/1994		
JP	10-046366		2/1998		
JP	10-83817		3/1998		
JP	10-199524		7/1998		
JP	10-199524	A	7/1998		
JP	2000-3727		1/2000		
JP	2000-173594		6/2000		
JP	2000-348730	A	12/2000		
JP	2001-291514		10/2001		
JP	2002-279974	A	9/2002		
JP	2002260637		9/2002		
JP	2002-313319	A	10/2002		
JP	2002-313345	A	10/2002		
JP	2002313319	*	10/2002	....	H01M 4/02
JP	2003313319	*	10/2002	....	H01M 4/02
JP	2003-017040		1/2003		
JP	2003-168426		6/2003		
JP	2003168426		6/2003		
JP	2003522367		7/2003		
JP	04-607488		2/2004		
JP	2004-71305		3/2004		
JP	2004-095264		3/2004		
JP	2004-214054		7/2004		
JP	2004-281317		10/2004		
JP	2004-296386	A	10/2004		
JP	2004-533699	A	11/2004		
JP	2004-533699	A	11/2004		
JP	2005-310759	A	11/2005		
JP	2006-505901	A	2/2006		
JP	2006-276214	A	10/2006		
JP	2006-290938	A	10/2006		
JP	2006-335410	A	12/2006		
JP	2007-165079	A	6/2007		
JP	2008-034266		2/2008		
JP	2008-186732		8/2008		
JP	2008-234988		10/2008		
JP	2009-252348	A	10/2009		
KR	2007-023141		2/2007		
KR	2007-0110569	A	11/2007		
KR	2008-038806	A	5/2008		
NL	1015956		8/2000		
SU	471402		5/1975		
SU	544019		1/1977		
WO	WO 99/33129		7/1999		
WO	WO 01/13414	A1	2/2001		
WO	WO 01/35473	A1	5/2001		
WO	WO 01/96847	A1	12/2001		
WO	WO 01/96847	A1	12/2001		
WO	WO 02/25356	A2	3/2002		
WO	WO 02/47185	A2	6/2002		
WO	WO 03/063271	A1	7/2003		
WO	WO 03/075372	A2	9/2003		
WO	WO 2004/042851	A2	5/2004		
WO	WO 2004/052489	A2	6/2004		
WO	WO 2004/083490	A2	9/2004		
WO	WO 2005/011030	A1	2/2005		
WO	WO 2005/113467	A1	12/2005		
WO	WO 2005/119753	A2	12/2005		
WO	WO 2006/067891	A1	6/2006		
WO	WO 2006/073427	A2	7/2006		
WO	WO 2006/120332	A2	11/2006		
WO	WO 2007/044315	A1	4/2007		
WO	WO 2007/083152		7/2007		
WO	WO 2007/083155		7/2007		
WO	WO 2007/083155	A1	7/2007		
WO	WO 2007083155	*	7/2007	....	H01M 4/38
WO	WO 2007/114168	A1	10/2007		
WO	WO 2007/136164	A1	11/2007		
WO	WO 2008/029888	A1	3/2008		
WO	WO 2008/044683	A1	4/2008		
WO	WO 2008/072460	A1	6/2008		
WO	WO 2008/097723	A1	8/2008		
WO	WO 2008/139157	A1	11/2008		
WO	WO 2009/010757		1/2009		
WO	WO 2009/010758		1/2009		
WO	WO 2009/010759		1/2009		
WO	WO 2009/026466		2/2009		
WO	WO 2009/120404	A1	10/2009		
WO	WO 2009/128800		10/2009		
WO	WO 2010/040985		4/2010		
WO	WO 2010/040986		4/2010		
WO	WO 2010/060348	A1	6/2010		
WO	WO 2010/130975	A1	11/2010		
WO	WO 2010/130976	A1	11/2010		

OTHER PUBLICATIONS

Chen et al., Binder Effect on Cycling Performance of Silicon/Carbon Composite Anodes for Lithium Ion Batteries, 36 (2006) 1099-1104.

Chen et al., "Effect of Vinylene Carbonate (VC) as Electrolyte Additive on Electrochemical Performance of Si Film Anode for Lithium Ion Batteries", Journal of Power Sources, 174(2), 538-543, (2007).

Chevrier et al., "Methods for Successful Cycling of Alloy Negative Electrodes in Li-Ion Cells", 220th ECS Meeting, Abstract #1237 (2011).

Choi et al., "Effect of Fluoroethylene Carbonate Additive on Interfacial Properties of Silicon Thin-Film Electrode", Journal of Power Sources, 161(2), 1254-1259 (2006).

El Ouatani et al., "The Effect of Vinylene Carbonate Additive on Surface Film Formation on Both Electrodes in Li-Ion Batteries", J. Electrochem. Soc., 156(2), A103-A113 (2009).

Han et al., "Neutralized Poly (Acrylic Acid) as Polymer Binder for High Capacity Silicon Negative Electrodes", 220th ECS Meeting, Abstract #1250 (2011).

Heinze et al., "Viscosity Behaviour of Multivalent Metal Ion-Containing Carboxymethyl Cellulose Solutions", Die Angewandte Makromolekulare Chamie 220, 123-132, (Nr. 3848), (1994).

Hochgatterer et al., "Silicon/Graphite Composite Electrodes for High Capacity Anodes: Influence of Binder Chemistry on Cycling Stability", Electrochemical and Solid-State Letters, 11 (5) (2008) A76-A80.

Komba et al., "Functional Interface of Polymer Modified Graphite Anode", Journal of Power Sources, 189, (2009), 197-203.

Komba et al., "Polyacrylate as Functional Binder for Silicon and Grapite Composite Electrode in Lithium-Ion Batteries", Electrochemistry, 79(1), (2011), 6-9.

(56) **References Cited**

OTHER PUBLICATIONS

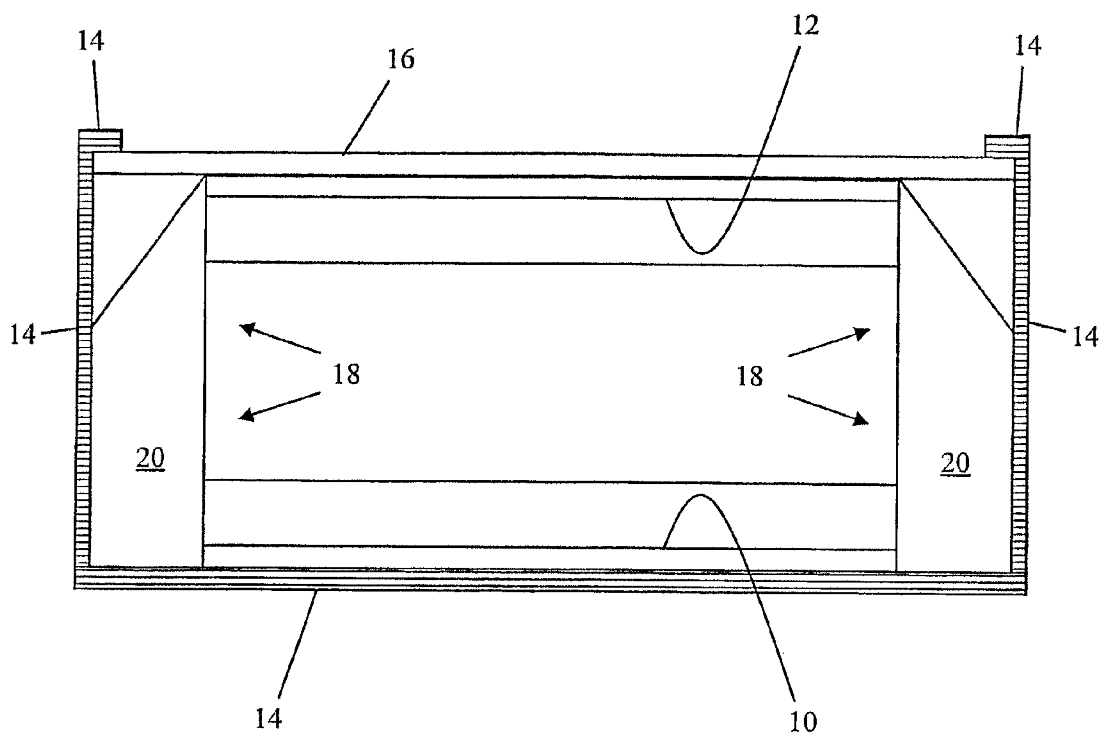
Komba et al., "Polyacrylate Modifier for Graphite Anode of Lithium-Ion Batteries", Electrochemical and Solid-State Letters, 12(5), (2009), A107-A110.
Komba et al., "Study on Polymer Binders for High-Capacity SiO Negative Electrode of Li-Ion Batteries", Journal of Physical Chemistry, 115, (2011), 13487-13495.
Lee et al., "Effect of Poly (Acrylic Acid) on Adhesion Strength and Electrochemical Performance of Natural Graphite Negative Electrode for Lithium-Ion Batteries", Journal of Power Sources, 161(1) (2006), 612-616.
Li et al., "Sodium Carboxymethyl Cellulose: A Potential Binder for Si Negative Electrodes for Li-Ion Batteries", Electrochemical and Solid-State Letters, 10(2) (2007), A17-A20.
Liu et al., "Enhanced Cycle Life of Si Anode for Li-Ion Batteries by Using Modified Elastomeric Binder", Electrochemical and Solid-State Letters, 8(2) (2005), A108-A103.
Obrovac et al., "Structural Changes in Silicon Anodes During Lithium Insertion/Extraction", Electrochemical and Solid-State Letters, 7(5), (2004), A96-A96.
Sugama, et al., "Nature of Interfacial Interaction Mechanisms Between Polyacrylic Acid Macromolecules and Oxide Metal Surfaces", Journal of Materials Science, 19 (1984) 4045-4056.
Ui et al., "Improvement of Electrochemical Characteristics of Natural Graphite Negative Electrode Coated With Polyacrylic Acid in Pure Propylene Carbonate Electrolyte", Journal of Power Sources, 173(1), (2007), 518-521.
Wen et al., "Chemical Diffusion in Intermediate Phases in the Lithium—Silicon System", Journal of Solid State Chemistry, 37 (1981) 271-278.
Weydanz et al., "A Room Temperature Study of the Binary Lithium—Silicon and the Ternary Lithium—Chromium—Silicon System for use in Rechargeable Lithium Batteries", Journal of Power Sources, 81-82 (1999) 237-242.
Yabuuchi et al., "Graphite-Silicon-Polyacrylate Negative Electrodes inIonic Liquid Electrolyte for Safer Rechargeable Li-Ion Batteries", Advanced Energy Materials, 1, (2011), 759-765.
Zhang et al., "A Review on Electrolyte Additives for Lithium-Ion Batteries", Journal of Power Sources, 162(2), 1379-1394, (2006).
Key to Metal Aluminum—Silicon Alloys, www.keytometals.com/Article80.
Peng et al., "Uniform, Axial-Orientation Alignment of One-Dimensional Single-Crystal Silicon Nanostructure Arrays", Angew. Chem. Ind. Ed., 44 (2005) 2737-2742.
Peng et al., "Simultaneous Gold Deposition and Formation of Silicon Nanowire Arrays", Journal of Electroanalytical Chemistry, 558 (2003) 35-39.
Canham, L. T., "Diffusion of Li IN Si", Properties of Silicon, EMIS Datareviews Series No. 4 (1987) 454-462.
Qiu et al., "Self-Assembled Growth and Optical Emission of Silver-Capped Silicon Nanowires", Applied Physics Letters, vol. 84, No. 19, (2004) 3867-3869.
Kim et al., "(110) Silicon Etching for High Aspect Ratio Comb Structures", 1997 6th International Conference on Emerging Technologies and Factory Automation Proceedings, (1997) 248-252.
Sharma et al., "Thermodynamic Properties of the Lithium—Silicon System", J. Electrochem. Soc.: Electrochemical Science and Technology, vol. 123 (1976) 1763-1768.
Qiu et al., "From S1 Nanotubes to Nanowires: Synthesis, Characterization, and Self-Assembly", Journal of Crystal Growth, 277 (2005) 143-148.
Tokoro et al., "Anisotropic Etching Properties of Silicon in KOH and TMAH Solutions", Proceedings of the 1998 International Symposium on Micromechatronics and Human Science (1998) 65-70.
Tsuchiya et al., "Structural Fabrication Using Cesium Chloride Island Arrays as a Resist in a Fluorocarbon Reactive Ion Etching Plasma", Electrochemical and Solid-State Letters, 3 (1) (2000) 44-46.
Wagner et al., "Vapor-Liquid-Solid Mechanism of Single Crystal Growth", Applied Physics Letters, vol. 4, No. 5 (1964) 89-90.
Lang, Walter, "Silicon Microstructuring Technology", Materials Science and Engineering, R17 (1996) 1-55.
Liu et al., "Effect of Electrode Structure on Performance of Si Anode in Li-Ion Batteries: Si Particle Size and Conductive Additive", Journal of Power Source, 140 (2005) 139-144.
Yan et al., "H_2-Assisted Control Growth of Si Nanowires", Journal of Crystal Growth, 257 (2003) 69-74.
Liu et al., "A Novel Method of Fabricating Porous Silicon Material: Ultrasonically Enhanced Anodic Electrochemical Etching", Solid State Communications, 127 (2003) 583-588.
Zhang et al., "Bulk-Quantity Si Nanowires Synthesized by SiO Sublimation", Journal of Crystal Growth, 212 (2000) 115-118.
Wong et al., "Controlled Growth of Silicon Nanowires Synthesized via Solid-Liquid-Solid Mechanism", Science and Technology of Advanced Materials, 6 (2005) 330-334.
Zhang et al., "Synthesis of Thin Si Whiskers (Nanowires) Using $SiCl_4$", Journal of Crystal Growth, 2006 (2001) 185-191.
Yoshio et al., "Electrochemical Behaviors of Silicon Based Anode Material", Journal of Power Sources, 153 (2006) 375-379.
Zhang et al., "Catalytic Growth of x-$FiSi_2$ and Silicon Nanowires", Journal of Crystal Growth, 280 (2005) 286-291.
Colinge, Jean-Pierre, "Silicon-on-Insulator Technology: Materials to VLSI", Chapter 2, SOI Materials, (1991), Cover page and p. 38.
Deal et al., "General Relationship for the Thermal Oxidation of Silicon", Journal of Applied Physics, vol. 36, No. 12, (Dec. 1965) 3770-3778.
Feng et al., "Lithography-Free Silicon Micro-Pillars as Catalyst Supports for Microfabricated Fuel Cell Applications", Electrochemistry Communications, 8 (2006) 1235-1238.
Green et al., "Quantum Pillar Structures on n+ Gallium Arsenide Fabricated Using "Natural" Lithography", Appl. Phys. Lett., 62 (3) (1993) 264-266.
Green et al., "Structured Silicon Anodes for Lithium Battery Applications", Electrochemical and Solid-State Letters, 6 (5) (2003) A75-A79.
Green et al., "Mesoscopic Hemisphere Arrays for use as Resist in Solid State Structure Fabrication", J. Vac. Sci. Technol. B 17(5) (1999) 2074-2083.
Yan et al., "Growth of Amorphous Silicon Nanowires via a Solid-Liquid-Solid Mechanism", Chemical Physics Letters, 323 (2000) 224-228.
Shin et al., "Porous Silicon Negative Electrodes for Rechargeable Lithium Batteries", Journal of Power Sources, 139 (2005) 314-320.
Li et al., "A High Capacity Nano-Si Composite Anode Material for Lithium Rechargeable Batteries", Electrochemical and Solid-State Letters, 2 (11) (1999) 547-549.
Li et al., "The Crystal Structural Evolution of Nano-Si Anode Caused by Lithium Insertion and Extraction at Room Temperature", Solid State Ionics, 135 (2000) 181-191.
Huggins, Robert A., "Lithium Alloy Anodes" in Handbook of Battery Materials, J.O. Besenhard Ed., Wiley-VCH, Weinheim, 361-381 (1999).
Chang et al., "Ultrafast Growth of Single-Crystalline Si Nanowires", Materials Letters, 60 (2006) 2125-2128.
Kim et al., "Improvement of Silicon Powder Negative Electrodes by Copper Electroless Deposition for Lithium Secondary Batteries", Journal of Power Sources, 147 (2005) 227-233.
Jianfeng et al., "Large-Scale Array of Highly Oriented Silicon-Rich Micro/Nanowires Induced by Gas Flow Steering", Solid State Communications, 133 (2005) 271-275.
Lu et al., "A Study of the Mechanisms of Erosion in Silicon Single Crystals Using Hertzian Fracture Tests", Wear, 186-187 (1995) 105-116.
Kleimann et al., "Formation of Wide and Deep Pores in Silicon by Electrochemical Etching", Materials Science and Engineering, B69-70 (2000) 29-33.
Kolasinski, Kurt W., "Silicon Nanostructures from Electroless Electrochemical Etching", Current Opinion in Solid State and Materials Science, 9 (2005) 73-83.
Pei et al., "Silicon Nanowires Grown from Silicon Monoxide Under Hydrothermal Conditions", Journal of Crystal Growth, 289 (2006) 423-427.

(56) **References Cited**

OTHER PUBLICATIONS

Chen et al., “Selective Etching of Silicon in Aqueous Ammonia Solution”, Sensors and Actuators, A 49 (1995) 115-121.
Maranchi et al., “Interfacial Properties of the a-Si/Cu:Active-Inactive Thin-Film Anode Systems for Lithium-Ion Batteries”, Journal of the Electrochemical Society: 153 (6) (2006) A1246-A1253.
Nakahata et al., “Fabrication of Lotus-Type Porous Silicon by Unidirectional Solidification in Hyrdogen”, Materials Science and Engineering A 384 (2004) 373-376.
Niparko, J.K. (Editor), “Cochlear Implant Technology”, Pub., Lippincott Williams and Wilkins, Philadelphia, (2000) 108-121.
Ohara et al., “A Thin Film Silicon Anode for Li-Ion Batteries Having a Very Large Specific Capacity and Long Cycle Life”, Journal of Power Sources, 136 (2004) 303-306.
Peng et al., “Dendrite-Assisted Growth of Silicon Nanowires in Electroless Metal Deposition”, Adv. Funct. Mater., 13, No. 2 (2003) 127-132.
Peng et al., “Synthesis of Large-Area Silicon Nanowire Arrays via Self-Assembling Nanoelectrochemistry”, Adv. Mater., 14, No. 16 (2002) 1164-1167.
Winter, et al., “Insertion Electrode Materials for Rechargeable Lithium Batteries”, Advanced Materials, 1998, 10, No. 10.
Kasavajjula et al., “Nano- and Bulk-Silicon-Based Insertion Anodes for Lithium-Ion Secondary Cells”, Journal of Power Sources, 163 (2007) 1003-1039.
Peng, et al., “Fabrication of Single-Crystalline Silicon Nanowires by Scratching a Silicon Surface with Catalytic Metal Particles”, Adv. Funct. Mater., 16 (2006), 387-394.
Barraclough et al., “Cold Compaction of Silicon Powders Without a Binding Agent”, Materials Letters 61 (2007) 485-487.
International Search Report for PCT/GB2008/001604 dated Aug. 27, 2008.
Written Opinion of the International Searching Authority dated Aug. 27, 2008.
Badel et al., “Formation of Ordered Pore Arrays at the Nanoscale by Electrochemical Etching of N-Type Silicon”, Superlattices and Microstructures, 36 (2004) 245-253.
Beaulieu et al., “Colossal Reversible Volume Changes in Lithium Alloys”, Electrochemical and Solid-State Letters, 4 (9) (2001) A137-A140.
Beaulieu et al., “Reaction of Li with Grain-Boundary Atoms in Nanostructured Compounds”, Journal of the Electrochemical Society, 147 (9) (2000) 3206-3212.
Besenhard et al., “Will Advanced Lithium-Alloy Anodes Have a Chance in Lithium-Ion Batteries?”, Journal of Power Sources, 68 (1997) 87-90.
Boukamp et al., “All-Solid Lithium Electrodes with Mixed-Conductor Matrix”, J. Electrochem. Soc.: Electrochemical Science and Technology, vol. 128, No. 4, (1981) 725-729.
Bourderau, et al., “Amorphous Silicon as a Possible Anode Material for Li-Ion Batteries”, Journal of Power Sources, 81-82 (1999) 233-236.
Ivanovskaya et al., “The Effect of Treatment of Cation-Selective Glass Electrodes With AgNO3 Solution on Electrode Properties”, Sensors and Actuators B 24-25 (1995) 304-308.
Peng et al., “Fabrication of Large-Area Silicon Nanowire p-n Junction Diode Arrays”, Adv. Mater. (2004), vol. 16, No. 1, 73-76.
Peng et al., “Silicon Nanowires for Rechargeable Lithium-ion Battery Anodes”, Applied Physics Letters (2008) vol. 93, No. 3, pp. 33105-1 to 33105-3.
De Angelis et al., “Water Soluble Nanoporous Nanoparticles for In Vivo Targeted Drug Deliver and Controlled Release in B Cells Tumor Context”, Nanoscale, 1020, vol. 2, p. 2230-2236.
Garrido, et al., The Role of Chemical Species in the Passivation of <100> Silicon Surfaces by HF in Water-Ethanol Solutions, J. Electrochem Soc., vol. 143, No. 12, 1996, p. 4059-4066.
Russo, et al., “A Mechanochemical Approach to Porous Silicon Nanoparticles Fabrication”, Materials 2011, vol. 4, p. 1023-1033.
Takami et al., “Silicon Fiber Formed on Silicon Without Using a Gas Process”, Journal of Applied Physics, vol. 91, No. 12, 2-5 (2002).
Ye et al., Controllable Growth of Silver Nanostructures by a Simple Replacement Reaction and Their SERS Studies, Solid State Sciences 11 (2009), p. 1088-1093.

* cited by examiner


14
16
12
14
14
14
18
18
20
20
14
10

SILICON ANODE FOR A RECHARGEABLE BATTERY

This invention relates to an electrode for a rechargeable battery cell that uses silicon or a silicon-based material as its active ingredient, in particular although not exclusively for use as the anode in a lithium-ion battery cell.

The recent increase in the use of portable electronic devices such as mobile telephones and notebook computers has created a need for smaller, lighter, longer lasting rechargeable batteries to provide the power to the above mentioned and other battery powered devices. During the 1990s, lithium rechargeable batteries, specifically lithium-ion batteries, became popular and, in terms of units sold, now dominate the portable electronics marketplace. However, as more and more power hungry functions are added to the above mentioned devices (e.g. cameras on mobile phones), improved batteries that store more energy per unit mass and per unit volume are required.

It is well known that silicon can be used as the active anode material of a rechargeable lithium-ion electrochemical battery cell (see, for example, Insertion Electrode Materials for Rechargeable Lithium Batteries, M. Winter, J. O. Besenhard, M. E. Spahr, and P. Novuk in Adv. Mater. 1998, 10, No. 10). The basic composition of a conventional lithium-ion rechargeable battery cell is shown in FIG. **1** including a graphite-based anode electrode, the component to be replaced by the silicon-based anode. The battery cell includes a single cell but may also include more than one cell.

The battery cell generally comprises a copper current collector for the anode **10** and an aluminium current collector for the cathode **12** which are externally connectable to a load or to a recharging source as appropriate. A graphite-based composite anode layer **14** overlays the current collector **10** and a lithium containing metal oxide-based composite cathode layer **16** overlays the current collector **12**. A porous plastic spacer or separator **20** is provided between the graphite-based composite anode layer **14** and the lithium containing metal oxide-based composite cathode layer **16** and a liquid electrolyte material is dispersed within porous plastic spacer or separator **20**, the composite anode layer **14** and the composite cathode layer **16**. In some cases, the porous plastic spacer or separator **20** may be replaced by a polymer electrolyte material and in such cases the polymer electrolyte material is present within both the composite anode layer **14** and the composite cathode layer **16**.

When the battery cell is fully charged, lithium has been transported from the lithium containing metal oxide via the electrolyte into the graphite-based layer where it reacts with the graphite to create the compound, LiC_6. The graphite, being the electrochemically active material in the composite anode layer, has a maximum capacity of 372 mAh/g. It will be noted that the terms “anode” and “cathode” are used in the sense that the battery is placed across a load.

It is generally believed that silicon, when used as an active anode material in a lithium-ion rechargeable cell, provides a significantly higher capacity than the currently used graphite. Silicon, when converted to the compound $Li_{21}Si_5$ by reaction with lithium in an electrochemical cell, has a maximum capacity of 4,200 mAh/g, considerably higher than the maximum capacity for graphite. Thus, if graphite can be replaced by silicon in a lithium rechargeable battery the desired increase in stored energy per unit mass and per unit volume can be achieved.

Existing approaches of using a silicon or silicon-based active anode material in a lithium-ion electrochemical cell have failed to show sustained capacity over the required number of charge/discharge cycles and are thus not commercially viable.

One approach disclosed in the art uses silicon in the form of a powder (say as particles or spherical elements with a 10 μm diameter), in some instances made into a composite with or without an electronic additive and containing an appropriate binder such as polyvinylidene difluoride coated onto a copper current collector. However, this electrode system fails to show sustained capacity when subjected to repeated charge/discharge cycles. It is believed that this capacity loss is due to partial mechanical isolation of the silicon powder mass arising from the volumetric expansion/contraction associated with lithium insertion/extraction to and from the host silicon. In turn this gives rise to electrical isolation of the silicon elements from both the copper current collector and themselves. In addition, the volumetric expansion/contraction causes the spherical elements to be broken up causing a loss of electrical contact within the spherical element itself.

Another approach known in the art designed to deal with the problem of the large volume changes during successive cycles is to make the size of the silicon elements that make up the silicon powder very small, that is to use spherical particles that have diameters in the 1-10 nm range. This strategy assumes that the nano-sized elements can undergo the large volumetric expansion/contraction associated with lithium insertion/extraction without being broken up or destroyed. However, this approach is problematic in that it requires the handling of very fine, nano-sized powder that may pose a health and safety risk and it does not prevent the electrical isolation of the spherical elements from both the copper current collector and themselves as the silicon powder undergoes the volumetric expansion/contraction associated with lithium insertion/extraction. Importantly, since a lithium-containing surface film is typically created during lithium insertion and the lithium ions that make up this surface film are trapped and can not be removed during the deinstertion process, the large surface area of the nano-sized elements can give introduce large irreversible capacity into the lithium-ion battery cell. In addition, the large number of small silicon particles creates a large number of particle-to-particle contacts for a given mass of silicon and these each have a contact resistance and may thus cause the electrical resistance of the silicon mass to be too high. The above problems have thus prevented silicon particles from becoming a commercially viable replacement for graphite in lithium rechargeable batteries and specifically lithium-ion batteries.

In another approach described by Ohara et al. in Journal of Power Sources 136 (2004) 303-306 silicon is evaporated onto a nickel foil current collector as a thin film and this structure is then used to form the anode of a lithium-ion cell. However, although this approach gives good capacity retention, this is only the case for very thin films (say ~50 nm) and thus these electrode structures do not give usable amounts of capacity per unit area. Increasing the film thickness (say >250 nm) causes the good capacity retention to be eliminated. The good capacity retention of these thin films is considered by the present inventors to be due to the ability of the thin film to absorb the volumetric expansion/contraction associated with lithium insertion/extraction from the host silicon without the film being broken up or destroyed. Also, the thin film has a much lower surface area than the equivalent mass of nano-sized particles and thus the amount of irreversible capacity due to the formation of a lithium-containing surface film is reduced. The above problems have thus prevented a thin film of silicon on a metal foil current collector from becoming a commercially viable replacement for graphite in lithium rechargeable batteries and specifically lithium-ion batteries.

In another approach described in U.S. Pat. No. 6,887,511, silicon is evaporated onto a roughened copper substrate to create medium-thickness films of up to 10 μm. During the initial lithium ion insertion process, the silicon film breaks up to form pillars of silicon. These pillars can then reversibly react with lithium ions and good capacity retention is achieved. However, the process does not function well with thicker films and the creation of the medium-thickness film is an expensive process, thus limiting this concept's commercially viability. Also, the pillared structure created by the break up of the film has no inherent porosity and thus the long terms capacity retention is questionable.

In another approach described in US2004/0126659, silicon is evaporated onto nickel fibres which are then used to form the anode of a lithium battery. However this is found to provide an uneven distribution of silicon on the nickel fibres hence significantly affecting operation. In addition, these structures have a high ratio of nickel current collector mass to active silicon mass and thus do not give usable amounts of capacity per unit area or per unit mass.

A review of nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells has been provided by Kasavajjula et al (J. Power Sources (2006), doi:10.1016/jpowsour.2006.09.84), herewith incorporated by reference herein.

The invention is set out in the independent claims.

Advantageously, some embodiments provide an electrode containing as its active material an interconnected array of high-aspect ratio silicon or silicon-based elements. Cycle life is improved as the structure of the elements, in conjunction with an upper limit of the smallest dimension of the elements, allows for accommodation of the volume expansion associated with insertion/extraction (charging and discharging) of the silicon or silicon-based elements while a lower limit on the smallest dimension controls the ratio of surface area for a given volume of silicon or silicon-based and thus minimises the surface-related irreversible capacity. At least one other dimension is chosen sufficiently large such as to ensure multiple contacts between elements for good electronic conductivity.

The high-aspect ratio elements may be elongate, for example ribbon-like such that a first larger dimension is larger than the smallest dimension and a second larger dimension is larger than the first larger dimension. High-aspect ratio elements may also be sheet-like or flake-like, wherein the first and second larger dimensions are larger than the first dimension but comparable to each other.

The invention is now described, by way of example only and with reference to the accompanying FIG. **1**, schematically showing a lithium ion rechargeable cell including an anode electrode in accordance with embodiments of the invention.

It has been realised by the inventors that the above-mentioned problems and drawbacks of the prior art may be addressed by carefully selecting the dimensions and geometry of the silicon or silicon-based elements that are the active ingredient of an electrode for a rechargeable battery. For elongate elements which have two comparable dimensions smaller than a third dimension (referred to as fibres in the remainder), to a first approximation, the irreversible capacity loss is inversely proportional to the diameter of the fibre. Similarly, for an elongate structure for which one of the two smaller dimensions is larger, than the other one, for example twice as large or more as the smaller dimension (referred to below as a ribbon) and for a element which has two comparable largest dimension and a single dimension smaller than that (referred to as a sheet or flake below) the irreversible capacity can be shown to be approximately inversely proportional to the thickness of the ribbon or sheet (that is the smallest dimension), ignoring the sides of the ribbon or the sheet. Thus, for fibres, ribbons, flakes or sheets, a ten-fold decrease in the smallest dimension approximately is expected to result in a ten-fold increase in the irreversible capacity loss. These considerations impose a lower limit on the smallest dimension for these structures if they are to be used as silicon elements in a composite electrode with limited irreversible capacity loss.

As discussed above, one significant problem in the use of silicon or silicon-based materials as the active anode material for a lithium-ion rechargeable battery cell is the large volume changes associated with the charging and discharging of the cell. The associated stresses lead to crack formation in bulk silicon; as described above. Experimental work on pillar-shaped silicon substrates has shown that silicon pillars of close to 1 micrometer diameter (approximately 0.8 micrometer) can be formed which can accommodate the volume changes without cracking [Mino Green, Elizabeth Fielder, Bruno Scrosati, Mario Wachtler and Judith Serra Moreno, "Structured Silicon Anodes for Lithium Battery Applications", Electrochemical and Solid-State Letters: 6, A75-A79 (2003).] Furthermore, experimental work on silicon plates has shown that even in thick plates (350 microns thickness) stress fractures have a characteristic length of 10 microns.

Based on the foregoing considerations, the smallest dimension of silicon or silicon-based elements in a electrode in accordance with an embodiment of the invention may be in the range of 0.08 to 1 preferably 0.2 μm to 0.3 μm or within the range therebetween. To further ensure a favourable surface area to volume ratio, the second largest dimension should be at least two times as large as the smallest dimension.

Another consideration is the number of electrical interconnections between the elements. For elongate elements such as fibres or ribbons, the larger the largest dimension, the more likely the individual members are to criss-cross each other and form multiple connections there between. Similarly, for sheet or flake-like members, the larger the flakes or sheets, the more likely they will be to mutually overlap. Moreover, the larger the one or two largest dimensions, the more mass of silicon will be arranged for a given surface area, further reducing irreversible capacity. Based on these considerations, the largest, or largest two dimensions are chosen to be larger than ten times the smallest dimension, preferable 100 or 200 times larger or within the range therebetween. The total length or largest dimension may be as large as 500 μm, for example.

It will be appreciated, of course, that any appropriate approach can be adopted in order to fabricate the silicon or silicon-based elements discussed above.

For example, fibres can be manufactured by forming pillars on a suitable silicon or silicon-based substrate and detaching these pillars to create fibres by a suitable method. Pillars of silicon can be manufactured as described in PCT/GB2007/000211 or as described in U.S. application Ser. No. 10/049,736.

Ribbons of silicon can be manufactured via a lithography process such that suitably shaped structure are made on a silicon or silicon-based substrate and then detached from the substrate using a suitable detachment method.

Sheets (or also flakes) may be manufactured using thin film deposition of silicon on poorly adhering substrates leading to detachable sheets of silicon. If the detachable sheet is broken up, flakes result.

Once the silicon or silicon-based elements have been manufactured they can be used as the active material in a composite anode for lithium-ion electrochemical cells. To fabricate a composite anode, the elements can be mixed with polyvinylidene difluoride and made into a slurry with a casting solvent such as n-methyl pyrrolidinone. This slurry can then be applied or coated onto a metal foil or other conducting substrate for example physically with a blade or in any other appropriate manner to yield a coated film of the required thickness and the casting solvent is then evaporated from this film using an appropriate drying system which may employ elevated temperatures in the range of 50 degrees C. to 140 degrees C. to leave the composite film free or substantially from casting solvent. The resulting composite film has a porous structure in which the mass of silicon or silicon-based elements is typically between 70 percent and 95 percent. The composite film will have a percentage pore volume of 10-30 percent, preferably about 20 percent.

Fabrication of the lithium-ion battery cell thereafter can be carried out in any appropriate manner for example following the general structure shown in FIG. **1** but with a silicon or silicon based active anode material rather than a graphite active anode material. For example the silicon elements-based composite anode layer is covered by the porous spacer **18**, the electrolyte added to the final structure saturating all the available pore volume. The electrolyte addition is done after placing the electrodes in an appropriate casing and may include vacuum filling of the anode to ensure the pore volume is filled with the liquid electrolyte.

A particular advantage of the approach described herein is that large sheets of silicon-based anode can be fabricated and then rolled or stamped out subsequently as is currently the case in graphite-based anodes for lithium-ion battery cells meaning that the approach described herein can be retrofitted with the existing manufacturing capability.

It will be appreciated, of course, that any appropriate approach can be adopted in order to arrive at the approaches and apparatus described above. For example the element manufacture can comprise any of a suitable method employed in the silicon processing industry. The cathode material can be of any appropriate material, typically a lithium-based metal oxide material. The elements can have any appropriate dimension and can for example be pure silicon or doped silicon or other silicon-based material such as a silicon-germanium mixture or any other appropriate mixture.

The above description is by way of example only and not intended to be limiting on the scope of the claimed subject matter which is intended to cover any such modifications, juxtapositions or alterations of the above-described embodiments as may appear to the skilled person. For example, although the specific description has been presented in terms of silicon as an electrode material, other silicon-based materials may be employed in place of undoped silicon, such as doped silicon, for example SiGe.

The present invention resulted from work undertaken under a joint research agreement between Nexeon Ltd and Imperial Innovations Ltd in the field of batteries, rechargeable cells and associated energy storage devices.

The invention claimed is:

1. An electrochemical cell anode comprising

a porous composite film containing a plurality of discrete silicon or silicon-based elements as an active material, each having a first dimension in the range of 0.08 μm to 0.3 μm and a second dimension of at least five times as large as the first dimension, the composite film having a mass of silicon or silicon-based elements between 70 and 95 percent,

wherein the silicon or silicon-based elements form an interconnected array,

wherein the silicon or silicon-based elements are capable of lithium insertion and removal, and

wherein the silicon or silicon-based elements are selected from the group consisting of hollow tubes, ribbons and flakes.

2. An electrochemical cell anode as claimed in claim **1**, in which the silicon or silicon-based elements are elongate.

3. An electrochemical cell anode as claimed in claim **1** further comprising a copper current collector.

4. An electrochemical cell containing an electrochemical cell anode as claimed in claim **1**.

5. An electrochemical cell as claimed in claim **4** in which a cathode of the electrochemical cell comprises lithium-based compound as its active material.

6. An electrochemical cell as claimed in claim **5** in which the cathode comprises lithium-based metal oxide as its active material.

7. A device powered by an electrochemical cell as claimed in claim **4**.

8. An electrochemical cell anode as claimed in claim **1** wherein the elements have a third dimension oriented transverse to each of the first and second dimensions, the third dimension being at least ten times as large as the first dimension.

9. An electrochemical cell anode as claimed in claim **1** wherein the elements have a third dimension oriented transverse to each of the first and second dimensions, the third dimension being at least 100 times as large as the first dimension.

10. An electrochemical cell anode as claimed in claim **1** wherein members of the interconnected array form multiple connections therebetween.

11. An electrochemical cell anode as claimed in claim **1** wherein members of the interconnected array criss-cross one another.

12. An electrochemical cell anode as claimed in claim **1** wherein the first dimension is in the range of 0.2 μm to 0.3 μm.

13. An electrochemical cell anode as claimed in claim **1** wherein the silicon or silicon-based elements are hollow tubes.

14. An electrochemical cell anode as claimed in claim **1** wherein the silicon or silicon-based elements are ribbons.

15. An electrochemical cell anode as claimed in claim **1** wherein the silicon or silicon-based elements are flakes.

16. An electrochemical cell anode as claimed in claim **1** wherein the second dimension is at least 10 times as large as the first dimension.

17. An electrochemical cell anode as claimed in claim **1** wherein the elements further comprise a third dimension that is at least 10 times as large as the first dimension.

18. An electrochemical cell anode as claimed in claim **4** further comprising an electrolyte saturating the available electrode pore volume.

19. A lithium-ion rechargeable battery cell containing an electrochemical cell anode as claimed in claim **1**.

20. An electrochemical anode as claimed in claim **1**, wherein the composite film has a pore volume between 10% and 30%.

21. An electrochemical cell as claimed in claim **6**, wherein the active material of the cathode comprises $LiCoO_2$.

22. An electrochemical anode as claimed in claim **1**, wherein the elements have a largest dimension that is no larger than 500 μm.

* * * * *